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Lattice Dynamics of Incommensurate Composite Rb-IV and a Realization of the Monatomic Linear Chain Model

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Longitudinal-acoustic (LA) phonons have been studied by inelastic x-ray scattering in the high-pressure incommensurate host-guest system Rb-IV in the pressure range of 16.3 to 18.4 GPa. Two LA-like phonon branches are observed along the direction of the incommensurate wave vector, which are attributed to separate lattice vibrations in the host and guest subsystems. The derived sound velocities for the host and the guest, v_h and v_g , respectively, are similar in magnitude [$v_h = v_g = 3840(100)$ m/s at 18 GPa], but our results indicate rather different pressure dependences of $dv_h/dP = 140(60)$ m/sGPa⁻¹ and $dv_g/dP = 280(80)$ m/sGPa⁻¹. The observations for the one-dimensional Rb guest chains are reproduced quantitatively on the basis of the monatomic linear chain model and the measured compressibility of the chains.

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In recent years, a number of surprisingly complex crystal structures has been discovered in the elements at high pressures, in particular, incommensurately modulated structures and incommensurate host-guest composite structures (see reviews [1] for an overview and references). The high-pressure phase rubidium-IV [2,3] shown in Fig. 1(a) belongs to the group of incommensurate host-guest structures that have also been observed in K, Ba, Sr, Sc, As, Sb, and Bi. Although considerable progress has been made in determining the detailed crystal structures of the complex metallic phases at high pressure, little is known about their other physical properties [4]. And while they have been investigated in theoretical studies [5], the mechanisms that lead to their formation and stability are not yet fully understood. The lattice dynamics of composite systems, which lack a conventional Brillouin zone due to the loss of translational symmetry along one or more crystal directions, have been addressed in model calculations [6–11], but only in the context of more complex incommensurate systems such as Hg_{3-δ}AsF₆ [12,13]. The 1D, monatomic nature of composite structures observed in the elements at high pressures offers the possibility of studying the lattice dynamics in much simpler systems.

Here we investigate the lattice dynamics in incommensurate composite Rb-IV by inelastic x-ray scattering (IXS). In particular, we focus on the longitudinal-acoustic (LA) phonons along the direction of the incommensurate wave vector (parallel to the guest-atom chains), which the calculations [6–11] predict to reflect the incommensurability most clearly. Rb-IV is stable from 16 to 20 GPa at room temperature. Above 16.7 GPa, both host and guest components exhibit long-range order, and the interchain long-range order is presumably mediated via minute distortions of the host lattice. Below 16.7 GPa the interchain correlation length decreases rapidly and is only ~ 40 Å at 16.1 GPa [14,15]. The breakdown of interchain correlations below 16.7 GPa suggests that the host-guest inter-

actions in Rb-IV are particularly weak. This view is supported by the fact that x-ray diffraction on Rb-IV yields extremely weak modulation reflections (which arise from the host-guest interactions), whereas they are readily observed in Sb-II, Sb-IV, and Bi-III [16].

The present study demonstrates that there are *two* well-defined LA-type phonon branches along the chain direction that can be attributed to separate LA excitations in the host and the guest sublattices. From the measured dispersion curves we have determined the sound velocities of these host and guest excitations as a function of pressure from 16.3 to 18.4 GPa. We find that the sound velocity

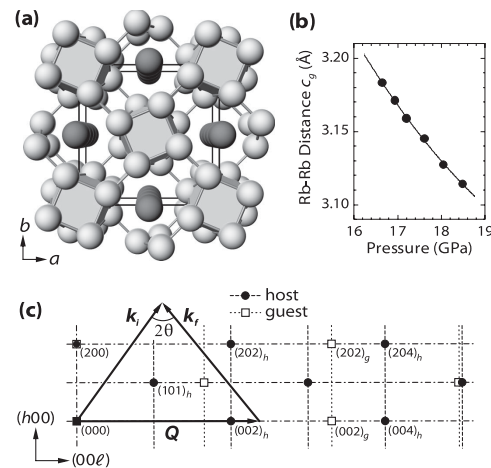


FIG. 1. (a) Crystal structure of Rb-IV [2,3]. It comprises a framework of “host” Rb atoms (light gray) with 1D channels that accommodate chains of “guest” Rb atoms (dark gray). The periodicities of the host and guest sublattices along the chain direction are incommensurate with each other. (b) Intrachain Rb-Rb distance vs pressure, $c_g(P)$. (c) The IXS scattering geometry. The circles and squares indicate the Bragg reflections, k_i and k_f , are the incoming and scattered photon wave vectors, and Q denotes momentum transfer vector.

along the guest-atom chains, and its pressure dependence, is in excellent agreement with that calculated using the monatomic linear chain model utilized in solid-state physics textbooks to introduce the concepts of lattice dynamics.

The IXS experiments were performed on beam line ID28 at the ESRF, Grenoble. The incident radiation was monochromatized at a photon energy of 17.794 keV. Two grazing-incidence mirrors focused the x rays onto the sample with a focal size of $25 \times 60 \mu\text{m}^2$. The spectrum of the scattered radiation was analyzed by a high-resolution spherical crystal (Si) analyzer to yield an overall energy resolution of 3 meV. The momentum resolution was set to 0.3 nm^{-1} and the IXS spectra were collected in the energy-scanning mode. The scattering geometry is shown in Fig. 1(c). A detailed account of the IXS setup has been given elsewhere [17].

An essential prerequisite for the present study was the ability to grow high-quality single crystals of Rb-IV in a diamond anvil cell (DAC), as described previously [15]. One Rb-IV crystal was investigated at a pressure of 18.4 GPa, while a second was studied at 17.3, 17.0, and 16.3 GPa. X-ray diffraction was used to confirm that both samples of Rb-IV were single crystals and to determine their crystal orientations within the DACs. The lattice parameters (a , $c_{\text{host}} \equiv c_h$, $c_{\text{guest}} \equiv c_g$) were determined *in situ* at the IXS beam line by scanning across three Bragg reflections. The sample pressures were derived from c_h and c_g on the basis of their previously measured pressure dependences [2,18].

Figure 2 shows selected IXS spectra recorded from Rb-IV at 17.3 GPa for three different momentum transfers Q . Despite the smallness of the sample in the DAC (scattering volume $\approx 2 \times 10^{-5} \text{ mm}^3$), high-quality spectra were obtained in $\sim 90 \text{ min}$. The spectra exhibit a clear Q dependence and comprise one or two inelastic features of varying energy and intensity in addition to the elastic line. We focus here on the LA excitations along the chain direction of Rb-IV by selecting momentum transfer vectors Q parallel to the crystal c axis [Fig. 1(c)] and taking advantage of the IXS selection rules. Also shown in Fig. 2 are decompositions of the measured spectra into the elastic line, the excitation peaks, and a constant background that were obtained by least-squares fitting [19]. The Stokes/anti-Stokes intensity ratios were assumed to be given by the Bose-Einstein population factors.

From the decompositions of the IXS spectra, the LA phonon energies were obtained as a function of momentum transfer (Fig. 3). The data points clearly separate into two dispersion branches. The first (solid symbols) exhibits the periodicity of the host lattice along the c direction. The apparent doubling of the periodicity originates from the body-centered nature of the host lattice. As shown by the solid line in Fig. 3, the dispersion relation is well modeled by a one-dimensional phonon dispersion relation of the type $\omega(q) = \sqrt{2\omega_0^2[1 - \cos(q\pi)]} = 2\omega_0|\sin(q\pi/2)|$, where ω_0 is the free-oscillator frequency. The second $E(q)$ data

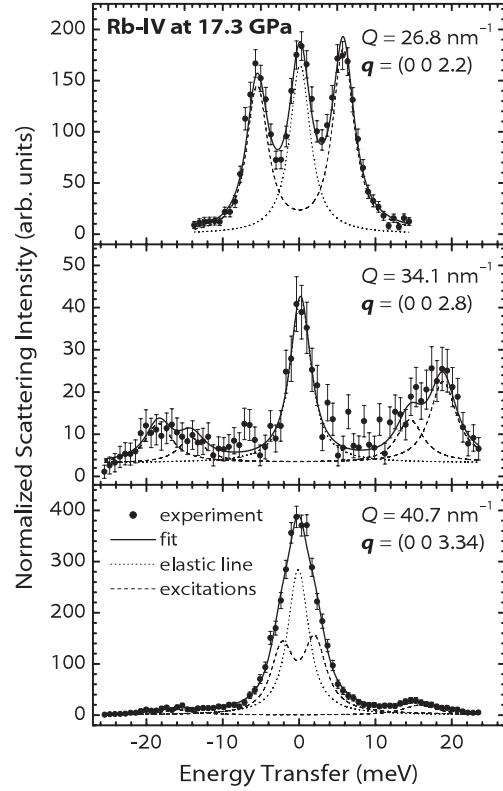


FIG. 2. IXS spectra of Rb-IV at 17.3 GPa ($T = 297 \text{ K}$). Spectra were recorded at different momentum transfers Q . The reduced wave vector q refers to the reciprocal lattice of the host, with a periodicity of $c_h = 5.1527 \text{ \AA}$ along the c direction. The circles indicate the measured intensities; the lines denote the fitted spectra and the contributing components. Note the different intensity scales for the three spectra.

set (open symbols) has a minimum at $(0 0 3.27)_h$ in the reciprocal lattice of the host, which corresponds to the $(002)_g$ lattice point of the guest structure. The intensity of these excitations decreases rapidly for momentum transfers away from the $(002)_g$ lattice point. The dominant features of the dynamical structure factor $S(Q, \omega)$ are two dispersion branches with the periodicity of the host and the guest lattice, respectively. They are thus assigned to separate LA-type phonon branches of the host and the guest sublattices. Further IXS data of Rb-IV were collected at 18.4, 17.0, and 16.3 GPa, yielding spectra and dispersion curves very similar to those shown in Figs. 2 and 3.

The appearance of two LA-type phonon branches along a certain crystal direction is a unique property of an incommensurate host-guest crystal [8–11]. In an idealized system of a host framework with embedded incommensurate chains, the two subsystems can slide relative to each other. This allows separate longitudinal phonons in the two sublattices, with polarization along the chain direction. In the limit of infinite wavelength, however, a crystal can have only one longitudinal-acoustic mode along the chain direction, which corresponds to a rigid translation of the entire crystal. In an incommensurate composite crystal, there exists a second mode with zero or nearly zero energy,

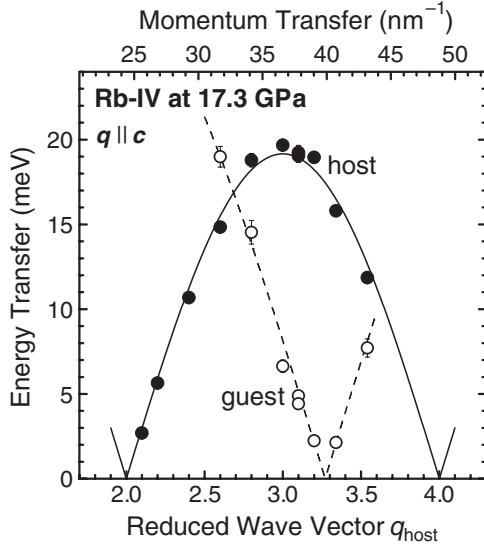


FIG. 3. Dispersion relations of LA lattice excitations in Rb-IV at 17.3 GPa. The reduced wave vector q (parallel to the chains) refers to the reciprocal lattice of the host. The two branches are attributed to lattice excitations of the host (solid symbols) and the guest (open symbols), respectively. The lines indicate phonon dispersion relations of the type $\omega(q) = \sqrt{2\omega_0^2[1 - \cos(q\pi)]}$ fitted to the data.

the phason, which corresponds to a rigid relative displacement of the two subsystems in opposite directions along the chains. There is thus a crossover from two separate LA-type phonon branches at high frequencies to two coupled excitations (the longitudinal-acoustic mode and the phason) at very low energies near the Brillouin zone center. In the case of $\text{Hg}_{3-\delta}\text{AsF}_6$, the crossover was estimated to occur at frequencies of the order of 1 MHz ($\approx 10^{-5}$ meV) [9], i.e., several orders of magnitude below the energy range accessible by IXS.

The theoretical aspects of the lattice dynamics of incommensurate composite systems have been studied in detail [6–11] in the context of the prototype host-guest compound systems $\text{Hg}_{3-\delta}\text{AsF}_6$ and alkane/urea, while experimental investigations have remained scarce. Recent numerical studies of various model systems with finite interaction between the subsystems indicate a complex structure of the dynamical structure factor $S(\mathbf{Q}, \omega)$ [6,20,21]: zone folding is believed to cause a multitude of dispersion branches that are separated by (pseudo-) gaps.

The dynamical structure factor of Rb-IV presented here is dominated by separate LA-like phonon branches of the host and the guest. Only a few of the IXS spectra indicate the possible existence of additional spectral weight that does not originate from the main phonon branches. These features were, however, extremely weak thus preventing their study in detail. Much stronger interaction between the host and guest is presumably required to observe deviations from the two-LA-branch scenario.

The high-frequency sound velocities (i.e., above the crossover from coupled to separate longitudinal modes)

in the host and guest structures (Fig. 4) were determined from the initial slopes of the fitted phonon dispersion relations. The sound velocities of the host and the guest, v_h and v_g , respectively, are rather similar in magnitude and their interpolated values are equal at a pressure of 18 GPa, $v_h = v_g = 3840(100)$ m/s. The speed of sound in the chains increases linearly at a rate of $dv_g/dP = 280(80)$ m/s GPa $^{-1}$, while the present data indicate a lower pressure dependence for the host, $dv_h/dP = 140(60)$ m/s GPa $^{-1}$. The sound velocities determined here for the guest chains are $\sim 10\%$ lower than the estimate derived recently from diffuse x-ray scattering of the disordered chains in the pressure range 16.2–16.4 GPa [15]. In view of the substantial challenges posed by the analysis of diffuse x-ray scattering data from a sample in a DAC, this is a good agreement, and it corroborates the analysis and model used in Ref. [15].

The present data provide no evidence of a significant change in the sound velocity along the chains below 16.7 GPa, the pressure at which the interchain correlation length begins to decrease rapidly [14,15]. As for the sound velocity in the host subsystem, we consider it unlikely that there is an anomaly at this pressure, given the lack of any measurable change in the crystal structure of the host at 16.7 GPa [18]. However, the results in Fig. 4 are not conclusive in this respect and further studies at a greater number of pressures would be needed to address these questions definitively.

As for the difference between the pressure dependences of the sound velocities of the host and the guest (while their absolute values are rather close), a simple ball-and-spring model of Rb-IV with one single spring constant for all nearest-neighbor interactions (without host-guest interaction) reproduces this situation semiquantitatively, including the larger compressibility of the chains. This suggests that the ratios of (i) the host and guest sound velocities along c , (ii) their pressure dependences, and (iii) the compressibilities along c are determined largely by geometrical factors, i.e., by the spatial arrangement of the atoms rather than details of the chemical bonding in the two subsystems.

The very weak coupling between the incommensurate host and the guest in Rb-IV raises a rather interesting question. Can the 1D chains of guest atoms in Rb-IV be considered a realization of the “monatomic linear chain” treated in textbooks (e.g., Ref. [22]) to introduce the concepts of crystal lattice dynamics? In order to calculate the sound velocity according to $v = d\sqrt{K_g/M}$ in the linear chain model, one needs to determine the force constant K_g and the atomic spacing $d \equiv c_g$ of the guest chains. K_g can be derived from the lattice parameter c_g measured as a function of pressure by x-ray diffraction [Fig. 1(b)]. One assumption needs to be made in order to calculate forces from c_g versus pressure, namely, on the effective cross sectional area of the chains. At 17.5 GPa, the minimum chain-host distance and the average distance between atoms in the chains are 3.11 and 3.15 Å, respectively, and

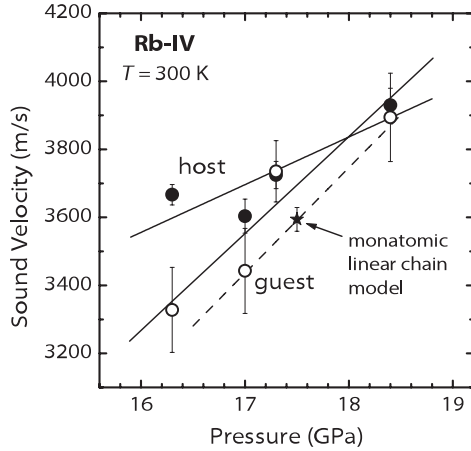


FIG. 4. Pressure dependences of the sound velocities of the LA phonons along the c directions of the host and the guest sub-system of Rb-IV. The solid lines represent linear regressions to the experimental data, and the error bars are derived from the uncertainties determined in the least-squares fitting of the phonon dispersion curves. The star and the dashed line indicate the estimated sound velocity and its pressure dependence in a monatomic linear chain of Rb.

the smallest tabulated value for the Rb^+ ionic radius is 1.48 Å [23,24]. We have therefore chosen an effective radius of $R = 1.50$ Å for the Rb chains. From x-ray diffraction measurements of the intrachain Rb-Rb distances, that is c_g , in the pressure range 16.6–18.5 GPa [Fig. 1(b)], a force constant of $K_g = -\pi R^2 dP/dc_g = 18.5(4)$ N/m is determined for the guest chains at 17.5 GPa. With $c_g = 3.1480(7)$ Å at the same pressure, one obtains a sound velocity of $v_g = 3594(35)$ m/s in the guest chains at $P = 17.5$ GPa, in excellent agreement with the guest sound velocity of 3700(100) m/s obtained by interpolating the measured data as shown in Fig. 4.

The success of the linear chain model encouraged us to estimate also the pressure dependence of v_g . The limiting factor in calculating this is the accuracy of the pressure derivative of K_g , since this requires the *second* pressure derivative of the lattice parameter c_g . As high-precision values of c_g could only be obtained from the diffractograms of single-phase and fully ordered Rb-IV between 16.6 and 18.5 GPa [Fig. 1(b)], d^2c_g/dP^2 is not very well constrained by the experiment. With $d^2c_g/dP^2 = 0.0038(14)$ Å/GPa², an estimate of $dv_g/dP = 310(140)$ m/s GPa⁻¹ is obtained, as indicated by the dashed line in Fig. 4, which is in good agreement with the measured pressure dependence, $dv_g/dP = 280(80)$ m/s GPa⁻¹. It can thus be concluded that the guest-atom chains in the composite Rb-IV structure do indeed represent a realization of the monatomic linear chain model with regard to the LA phonons.

In summary, we have reported the first experimental investigation of the lattice dynamics in an element with a

composite crystal structure. Two well-defined LA-type phonon branches are observed in Rb-IV along the direction of the incommensurate wave vector, which are assigned to separate LA-type phonons of the host and the guest sublattices. The LA phonons in the chains are well described by the classic monatomic linear chain model. The present observations motivate further studies in search for zone-folding effects and gaps in the dynamical structure factor $S(\mathbf{Q}, \omega)$, which are predicted by theory but have not been observed in the present work.

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